

PATENT SPECIFICATION

DRAWINGS ATTACHED

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Process for preparing high molecular weight polymers of α -olefins.

COMPLETE SPECIFICATION

We, MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, a Body Corporate, organised and existing under the Laws of the Republic of Italy, of 18 Via Filippo Turati, Milan, Italy, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

The present invention relates to an improved process for the production of high molecular weight polymers of α -olefins having a regular structure.

More particularly it relates to a continuous process for the production of said polymers.

In earlier Applications of the present Applicants there is described a batch process for obtaining these polymers, in which the organo-metallic compound which is one of the components of the catalyst, dissolved in a suitable solvent, is introduced into a reactor and the solvent is saturated with the amount of monomer to be polymerised, heating is then commenced the temperature of the solution being raised to 50-70°C and then the transition metal compound which initiates the polymerisation is introduced in one or more stages thus causing a temperature increase of about 10-20°C. After the established reaction time, methyl alcohol is introduced into the reactor in order to decompose the catalyst, the reactor is cooled, pressure is reduced to atmospheric and the polymer solution is discharged.

It has now been found that a more convenient process for the production of polymers of α -olefins consists in feeding in the monomer, the solvent and the two components of the catalyst continuously, and discharging the polymer solution and the unreacted monomer gas continuously. The gas, after a suitable addition of further monomer, in order to replace the amount consumed in the reaction, is recycled.

The invention provides a process for the production of high molecular weight polymers of α -olefins having at least three carbon atoms which olefins satisfy the general formula $R-CH=CH_2$ (where R is an alkyl, cyclo alkyl, cyclo alkenyl or aryl group), the polymers being linear, essentially unbranched, head-to-tail polymers, using under substantially anhydrous and oxygen-free conditions a catalyst prepared by contacting a crystalline compound of a metal of Group IVa, Va or VIa of the Periodic Table according to Mendeleeff in which its metal has a valency less than four and which compound is substantially insoluble in the polymerisation medium with a metal alkyl compound of aluminium or a metal of Group II of said Table, at a pressure of from 1 to 150 atmospheres and at a temperature of from 50 to 150°C in the presence of a hydrocarbon solvent, characterised in that the α -olefin monomer, a suspension of the catalyst and the hydrocarbon solvent are continuously fed in predetermined constant proportions to a reactor or two or more reactors connected in series, the formed polymer being continuously discharged and the solvent separated therefrom, said separated solvent and any unreacted monomer being recycled to said reactor or reactors. The process of the invention is particularly applicable to the polymerisation of propylene. Some of the advantages obtained by the continuous process of the invention which will be described in greater detail hereinafter, in comparison with the batch-process are as follows:

- (1) An improvement in the heat exchange and the reduction or elimination of thermal gradients in the reacting mass;
- (2) The possibility of operating in reactors without the need to provide mechanical stirrers;
- (3) The production of more homogeneous polymers having constant characteristics

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(particularly polymers with a lower molecular weight dispersion and with a well defined molecular weight):

(4) Better contact between the reaction phases:

(5) An increase of the yields:

The advantage of (3) above is to a large extent a result of (1) above because the temperature has a considerable influence on the molecular weight of the polymer.

It should be noted that temperature uniformity is assured not only by the continuous moving of the reaction mass but also by the fact that by continuously renewing the catalyst, its activity is kept constant, thus preventing reaction peaks with consequent developments of high temperatures.

The yield increase, on the other hand, depends mainly on the fulfilment of the condition of (1) above and, also on the continuous renewal of the catalyst. The gaseous monomer in fact always contains small amounts of moisture carbon monoxide, sulphur compounds and other impurities (i.e. substances which poison the catalyst). In the continuous process of this invention such impurities are destroyed in the first operating stage by reaction with the catalyst, and, therefore, the gas which is recycled is very pure. Due to the fact that only small amounts of gas are added in each cycle in order to replace the monomer consumed, it is evident that the amount of catalyst which is poisoned by the very small amounts of impurities is in fact very low.

The following is a description of two arrangements which have proved to be particularly suitable for carrying out the process of the present invention. Reference is made to the accompanying drawings in which Figures 1 and 2 are schematic representations of suitable arrangements.

According to Figure 1 the reactants (solvents, catalyst and α -olefin) suitably measured by rotary flow meters are continuously fed to a pre-polymerisation vessel 1, thermoregulated by a jacket and provided with a rotating mechanical stirrer, operating at a superatmospheric pressure (e.g. from 2 to 30 atmospheres) and at a temperature of from 50 to 150°C. A pump 9 supplies catalyst from a tank 4 to the vessel 1. The reaction mass is passed into a reactor-exhauster 2, operating under the same conditions as the vessel 1, into which a second monomer fraction, delivered from the pipe network, is introduced in order to exhaust any catalyst which is still active.

From reactor 2 the reaction suspension is delivered, (flow is regulated by means of a valve which is servo-controlled by timing means operating in conjunction with a manometer) to an expansion vessel, separator 3, in which the reaction suspension is sepa-

rated from unpolymerised monomer, a portion of which is collected in a gas holder 6 and recycled by means of a compressor 7, while another portion is discharged.

The gas free reaction suspension (consisting of the polymer, the solvent and the catalytic residues) which is separated in the separator 3, is discharged by a screw 10 and fed to a centrifuge 11 in which the solvent, which is recycled to tank 5 and then delivered to reactor 1 by a pump 8 is separated from the polymer which is then purified and dried.

Figure 2 illustrates a modified arrangement in which, instead of reactors 1 and 2, a single monotubular or polytubular reactor 6, provided with gas and liquid recycling means, is used, operating under temperature and pressure conditions similar to those described above, and to which the reactants, suitably measured by flowmeters, are fed continuously.

The reaction mixture passes from the reactor 6 to a separator 7, in which the unreacted monomer is separated and partially recycled through a gas holder 1 and compressor 2, while the gas free reaction suspension is fed to a centrifugal pump 5 and passes to a centrifuge 8, in which the polymer is separated from the solvent which, suitably added to fresh solvent, is recycled to reactor 6 through a tank 9 and pump 10 while the polymer is purified and dried. The heavy line below the reactor 6 in Figure 2 serves for completely discharging the reactor at the end of a run. Thus the valve (unnumbered) in this line is normally closed and the line serves for the catalyst contained in a tank 3 to be fed to the reactor by a pump 4. In both arrangements the catalyst is previously prepared by reaction of the two components, i.e. the metal alkyl compound with the compound of a metal of Group IVa, Va or VIa of the Periodic Table.

The following Examples are given to illustrate the invention.

EXAMPLE 1

To the reactors 1 and 2 of Figure 1 having a total capacity of 1000 litres, 100 kg propylene, 210 kg commercial heptane and 2 kg of a catalytic suspension of titanium trichloride and aluminium triethyl, diluted to 50% with heptane, are fed per hour under a pressure of 5 atmospheres. The reaction temperature is kept at about 70°C. 90 kg per hour of polypropylene (calculated as dry polymer) are obtained, while 6 kg per hour of non-reacted olefin and 200 kg per hour of solvent are recovered and recycled.

The olefin conversion is 90% and the polymerisation yield, calculated on the olefin actually consumed, is up to about 96%.

The yield on the catalyst is 90 g polymer per gram of catalyst. The solvent consump-

tion is about 5% of the heptane used. The output of two reactors connected in series is 0.09 kg polymer per hour and per litre of reactor.

5 EXAMPLE 2

To a 3-stage, hexa-tubular reactor 6, (Figure 2) having a capacity of 250 litres, 200 kg/h propylene, 700 kg/h commercial heptane and 3 kg/h of a catalytic 50% heptane suspension of titanium trichloride and aluminium triethyl are fed under a pressure of 10 atmospheres at 70°C. The reaction temperature is kept at about 75°C.

160 kg/h polypropylene (calculated as dry polymer) are obtained while 27 kg/h unpolymerised olefin and 670 kg/h solvent are recovered and recycled.

The olefin conversion is 80% and the polymerisation yield calculated on the olefin actually consumed is up to 98%. The yield on the catalyst is 106 g polymer per gram of catalyst.

The solvent consumption is about 4.5% of the heptane used. The output of the reactor is about 0.6 kg polymer per hour per litre.

WHAT WE CLAIM IS:—

1. A process for the production of high molecular weight polymers of α -olefins having at least three carbon atoms, which olefins satisfy the general formula $R-CH=CH_2$ (where R is an alkyl, cycloalkyl, cycloalkenyl or aryl group), the polymers being linear, essentially unbranched, head-to-tail polymers, using under substantially anhydrous and oxygen-free conditions a catalyst prepared by contacting a crystalline compound of a metal of Group IVa, Va or VIa of the

Periodic Table according go to Mendeleeff in which the metal has a valency less than four and which compound is substantially insoluble in polymerisation medium with a metal alkyl compound of aluminium or a metal of Group II of said Table, at a pressure of from 1 to 150 atmospheres and at a temperature of from 50 to 150°C in the presence of a hydrocarbon solvent, characterised in that the α -olefin monomer, a suspension of the catalyst and the hydrocarbon solvent are continuously fed in predetermined constant proportions to a reactor or two or more reactors connected in series, the formed polymer being continuously discharged and the solvent separated therefrom, said separated solvent and any unreacted monomer being recycled to said reactor or reactors.

2. A process according to Claim 1, wherein said monomer is propylene.

3. A process according to Claim 1 or Claim 2, wherein said solvent is *n*-heptane.

4. A process for the production of high molecular weight polymers of α -olefins, substantially as hereinbefore described and illustrated by the foregoing Examples:

5. High molecular weight polymers of α -olefins prepared by the process claimed in any one of the preceding Claims.

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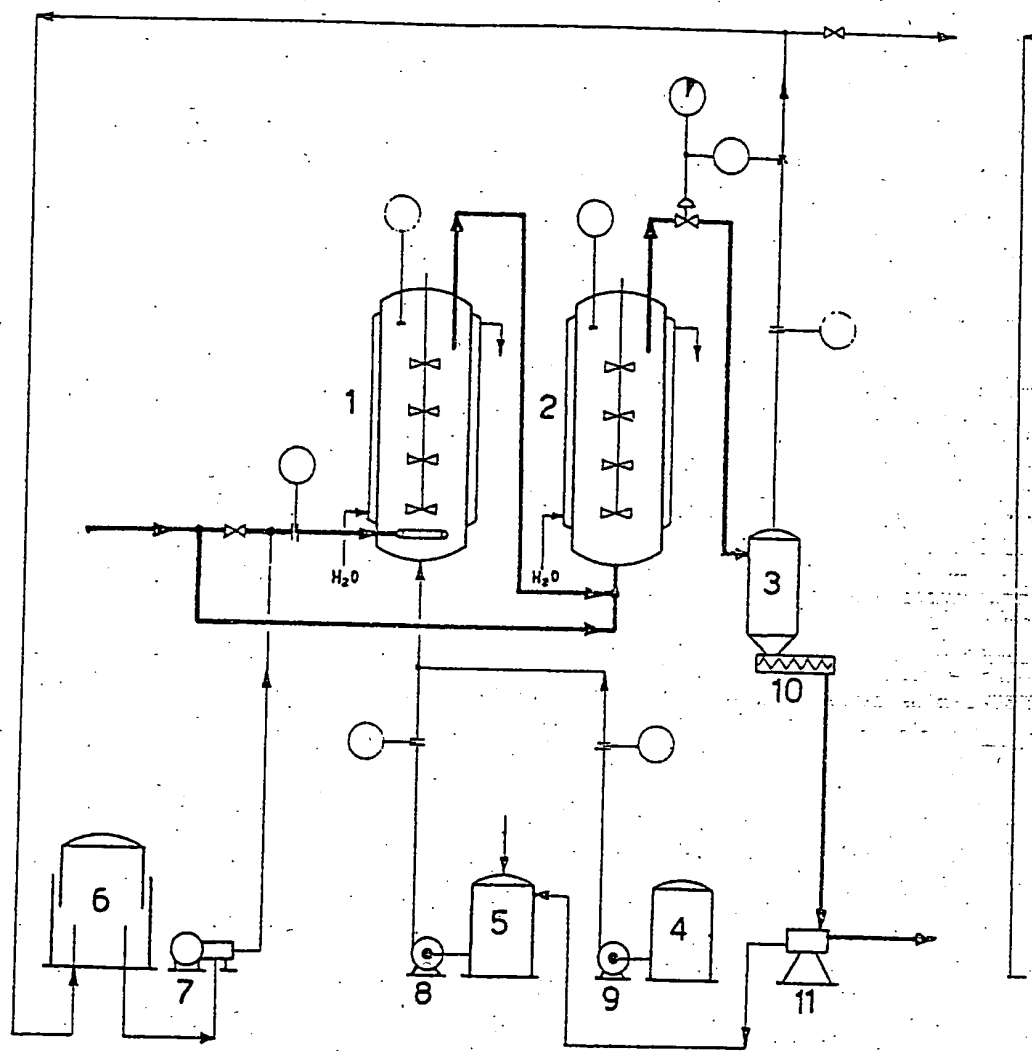


Fig. "1"

The diagram illustrates a water treatment system with two parallel filtration units, labeled 1 and 2. Each unit consists of a cylindrical filter vessel with internal components. Unit 1 has an inlet labeled H_2O and an outlet labeled H_2O . Unit 2 also has an inlet labeled H_2O and an outlet labeled H_2O . The outlets of both units feed into a common distribution line. This line branches out to various components: a pump (7) leading to a storage tank (6), a pump (8) leading to a storage tank (5), a pump (9) leading to a storage tank (4), and a pump (10) leading to a storage tank (3). The storage tank (3) has an outlet labeled 11. The system also includes several other pumps (3, 4, 5, 6, 7, 8, 9) and a network of pipes with valves and flow indicators.

Fig. 2.